

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 4/02, 10/00	A1	(11) International Publication Number: WO 98/44009 (43) International Publication Date: 8 October 1998 (08.10.98)
(21) International Application Number: PCT/EP98/01680 (22) International Filing Date: 23 March 1998 (23.03.98) (30) Priority Data: 97200932.8 29 March 1997 (29.03.97) EP (34) Countries for which the regional or international application was filed: NL et al. (71) Applicant: MONTELL TECHNOLOGY COMPANY B.V. [NL/NL]; Hoeksteen 66, NL-2132 MS Hoofddorp (NL). (72) Inventors: SACCHETTI, Mario ; Viale Krasnodar, 138, I-44100 Ferrara (IT). GOVONI, Gabriele ; Via Pilastro, 63, I-44045 Renazzo (IT). FAIT, Anna ; Via Arianuova, 56/B, I-44100 Ferrara (IT). (74) Agent: ZANOLI, Enrico ; Montell Italia S.p.A., Intellectual Property, Patents and Trademarks, Via Pergolesi, 25, I-20124 Milano (IT).	(81) Designated States: AU, BR, CA, CN, CZ, HU, ID, IL, JP, KR, MX, NO, RU, TR, UA , European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	
(54) Title: MAGNESIUM DICHLORIDE-ALCOHOL ADDUCTS, PROCESS FOR THEIR PREPARATION AND CATALYST COMPONENTS OBTAINED THEREFROM (57) Abstract <p>The present invention relates to $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$ adducts, where R is a $\text{C}_1\text{--C}_{10}$ alkyl, $2 \leq m \leq 4.2$, $0 \leq n \leq 0.7$, characterized by an X-ray diffraction spectrum in which, in the range of 2θ diffraction angles between 5° and 15°, the three main diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction lines being the one at $2\theta = 8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line. Catalyst components obtained from the adducts of the present invention are capable to give catalysts for the polymerization of olefins characterized by enhanced activity and stereospecificity with respect to the catalysts prepared from the adducts of the prior art.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

"MAGNESIUM DICHLORIDE-ALCOHOL ADDUCTS, PROCESS FOR THEIR PREPARATION AND CATALYST COMPONENTS OBTAINED THEREFROM"

The present invention relates to magnesium dichloride/alcohol adducts which are characterized by particular chemical and physical properties. The adducts of the present invention are particularly useful as precursors of catalyst components for the polymerization of olefins.

$\text{MgCl}_2 \cdot n\text{alcohol}$ adducts and their use in the preparation of catalyst components for the polymerization of olefins are well known in the art.

J.C.J. Bart and W. Roovers [Journal of Material Science, 30 (1995), 2809-2820] describe the preparation of a number of $\text{MgCl}_2 \cdot n\text{EtOH}$ adducts, with n ranging from 1.4 to 6, and their characterization by means of X-ray powder diffraction. A range of allegedly new adducts, with $n=6, 4.5, 4, 3.33, 2.5, 1.67, 1.50$ and 1.25 , is characterized in terms of X-ray diffraction pattern. According to the authors, the $\text{MgCl}_2 \cdot n\text{alcohol}$ adducts can be converted to active polymerization catalyst supports through the elimination of the alcohol molecules from the adducts by thermal desolvation. In table III of the article, the characteristic diffraction lines of the above indicated new adducts are reported with reference to the interplanar distances. For convenience, the same diffraction lines are reported below with reference to the 2θ diffraction angles;

limitedly to the range of 2θ diffraction angles between 5° and 15° (the relative intensity I/I_0 with respect to the most intense diffraction line is reported in brackets). For $n=1.25$: $2\theta=7.6^\circ$ (100), 12.28° (25), 14.9° (8); for $n=1.5$: $2\theta=8.44^\circ$ (100), 11.95° (48), 14.2° (46); for $n=1.67$: $2\theta=6.1^\circ$ (9), 6.68° (100), 8.95° (50), 9.88° (33), 11.8° (8), 12.28° (33), 14.5° (13), 14.75° (4); for $n=2.5$: $2\theta=6.3^\circ$ (27), 9.4° (100), 9.93° (70), 11.7° (11), 12.35° (6), 14.9° (6); for $n=3.33$: $2\theta=9.14^\circ$ (15), 9.44° (100), 11.88° (15), 12.9° (27); for $n=4$: $2\theta=8.7^\circ$ (49), 10.1° (73), 10.49° (100), 11.8° (58); for $n=4.5$: $2\theta=9.65^\circ$ (100), 11.4° (10), 12.5° (24), 12.94° (32), 14.25° (20), 14.95° (6); for $n=6$: $2\theta=8.94^\circ$ (100), 13.13° (3). A $\text{MgCl}_2 \cdot 2\text{EtOH} \cdot 0.5\text{H}_2\text{O}$ adduct is also reported, the diffraction lines of which in the relevant range are the following: $2\theta=7.9^\circ$ (35); 8.5° (>100); 9.7° (26); 11.32° (100); 12.59° (11); 13.46° (12).

Catalyst components for the polymerization of olefins, obtained by reacting $\text{MgCl}_2 \cdot n\text{EtOH}$ adducts with halogenated transition metal compounds, are described in USP 4,399,054. The adducts are prepared by emulsifying the molten adduct in an immiscible dispersing medium and quenching the emulsion in a cooling fluid to collect the adduct in the form of spherical particles. No X-ray characteristics of the adducts are reported.

USP 4,421,674 describes a method for preparing a catalyst component for the polymerization of olefins which involves the

preparation of $\text{MgCl}_2 \cdot \text{EtOH}$ adducts by means of the following steps: (a) preparation of a MgCl_2 solution in ethanol; (b) spray-drying said solution to collect particles of the adduct in spherical form, said adduct having from 1.5 to 20% by weight of residual alcoholic hydroxyl content and being characterized by an X-ray spectrum in which the maximum peak at 2.56° (i.e. $2\theta=35^\circ$) characteristics of the crystalline anhydrous MgCl_2 is practically absent and a new maximum peak at about 10.8° (i.e. $2\theta=8.15^\circ$) is present; lesser peaks at about 9.16° (i.e. $2\theta=9.65^\circ$) and 6.73° (i.e. $2\theta=13.15^\circ$) are also reported.

EP-A-700936 describes a process for producing a solid catalyst component for the polymerization of olefins which comprises the preparation of $\text{MgCl}_2 \cdot \text{EtOH}$ adducts by means of the following steps: (A) preparation of a mixture having formula $\text{MgCl}_2 \cdot m\text{ROH}$, wherein R is an alkyl group with 1 to 10 carbon atoms and $m=3.0$ to 6.0 ; (B) spray-cooling said mixture to obtain a solid adduct having the same composition as of the starting mixture; (C) partly removing the alcohol from the above-obtained solid adduct to obtain an adduct containing from 0.4 to 2.8 mol of alcohol per mol of MgCl_2 . The adduct obtained in (C) is characterized by an X-ray diffraction spectrum in which a novel peak does not occur at a diffraction angles $2\theta=7$ to 8° as compared with the diffraction spectrum of the adduct obtained in (B), or even if it occurs, the intensity of the novel peak

is 2.0 times or less the intensity of the highest peak present at the diffraction angles $2\theta=8.5$ to 9° of the diffraction spectrum of the adduct obtained in (C). Fig. 2 of the said European Patent Application shows a typical X-ray diffraction spectrum of the adducts prepared in (B). The highest peak occurs at $2\theta=8.8^\circ$; two less intense peaks occur at $2\theta=9.5$ to 10° and $2\theta=13^\circ$, respectively. Fig. 3 shows a typical X-ray diffraction spectrum of the adducts prepared in (C). The highest peak occurs at $2\theta=8.8^\circ$; other peaks occur at $2\theta=6.0$ to 6.5° , $2\theta=9.5$ to 10° and $2\theta=11$ to 11.5° . Fig. 4 shows a typical X-ray diffraction spectrum of comparative adducts prepared in (C). The highest peak occurs at $2\theta=7.6^\circ$; other peaks occur at $2\theta=8.8^\circ$, $2\theta=9.5$ to 10° , $2\theta=11$ to 11.5° and $2\theta=12$ to 12.5° .

A new $\text{MgCl}_2 \cdot \text{alcohol}$ adduct has now been found which is characterized by a particular X-ray diffraction spectrum, not shown by the adducts of the prior art, and/or by a particular crystallinity as shown by the Differential Scanning Calorimetry (DSC) profile of the adduct. In addition, particular $\text{MgCl}_2 \cdot \text{alcohol}$ adducts of the present invention can be characterized by their viscosity values in the molten state which, for a given alcohol content, are higher than the viscosity values of the corresponding adducts of the prior art. In addition to the alcohol, minor amounts of water can also be present in the adducts according to the invention.

The adducts of the present invention can be used to prepare catalyst components for the polymerization of olefins by reaction with transition metal compounds. Catalyst components obtained from the adducts of the present invention are capable to give catalysts for the polymerization of olefins characterized by enhanced activity and stereospecificity with respect to the catalysts prepared from the adducts of the prior art. Also, the morphological properties of the obtained polymers are improved, particularly when adducts in spherical forms are used.

The present invention therefore relates to $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$ adducts, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $2 \leq m \leq 4.2$, $0 \leq n \leq 0.7$, characterized by an X-ray diffraction spectrum in which, in the range of 2θ diffraction angles between 5° and 15° , the three main diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction lines being the one at $2\theta = 8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction line.

The above described diffraction pattern is unique and it has never been described in the prior art. In fact, none of the spectra reported in Bart et al. corresponds to the spectrum which characterizes the adducts of the present invention; the same applies to the adducts disclosed in EP-A-700936. As for

the adducts described in USP 4,399,054, applicants repeated the preparation of the adducts according to the procedure described therein. The X-ray diffraction spectrum of the obtained adduct shows, in the range of 2θ diffraction angles between 5 and 15° , the following main peaks (the relative intensity I/I_0 with respect to the most intense diffraction line is in brackets): $2\theta=8.84^\circ$ (79); $2\theta=9.2$ (100); $2\theta=9.43$ (68); $2\theta=9.82$ (19). Contrary to the adducts of the present invention, which are characterized, inter alia, by a most intense diffraction line occurring at $2\theta=8.8 \pm 0.2^\circ$, the adducts of USP 4,399,054 are characterized by a most intense diffraction line at $2\theta=9.2^\circ$.

Preferably R is a C_1 - C_4 alkyl, more preferably ethyl, m is between 2.2 and 3.8, more preferably between 2.5 and 3.5, n is between 0.01 and 0.6, more preferably between 0.001 and 0.4. The X-ray diffraction spectra are determined with reference to the main diffraction lines of silicon, used as an internal standard, using the apparatus and the methodology described hereinafter.

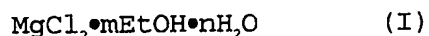
The preferred adducts of the present invention are characterized by an X-ray diffraction spectrum in which the intensity of the diffraction lines at $2\theta=9.4^\circ \pm 0.2^\circ$ and $9.8^\circ \pm 0.2^\circ$ is at least 0.4 times, preferably at least 0.5 times the intensity of the most intense diffraction line at $2\theta=8.8^\circ \pm 0.2^\circ$.

As an alternative, or in addition to the X-ray spectrum, the adducts of the present invention are characterized by a Differential Scanning Calorimetry (DSC) profile in which no peaks are present at temperatures below 90°C or, even if peaks are present below said temperature, the fusion enthalpy associated with said peaks is less than 30% of the total fusion enthalpy.

The DSC analysis is carried out using the apparatus and the methodology described hereinafter.

When R is ethyl, m is between 2.5 and 3.5 and n is between 0 and 0.4, the fusion enthalpy associated with peaks possibly present at temperatures below 90°C is less than 10% of the total fusion enthalpy. In said case the adducts are furthermore characterized by the fact that the maximum peak occurs at temperatures between 95 and 115°C.

Particularly preferred are adducts of the formula (I)



where m is between 2.2 and 3.8 and n is between 0.01 and 0.6, having both the above described X-ray spectrum and the above described DSC features. Adducts of this type can be further characterized by their viscosity in the molten state. In fact, it has been unexpectedly found that adducts with the above described features are also characterized by values of viscosity which, for a given alcohol content, are higher than

the values of viscosity of the corresponding adducts of the prior art. In particular, on a plot viscosity vs. EtOH molar content, the values of viscosity at 115°C (expressed in poise) of the adducts (I) are above the straight line passing through the points having, respectively, a viscosity/EtOH molar content of 2.43/2.38 and 1.26/3.31; at 120° the values of viscosity of the adducts (I) are above the straight line defined by the points having viscosity/EtOH molar content values of 1.71/2.38 and 0.9/3.31; at 125° the values of viscosity of the adducts (I) are above the straight line passing through the points defined by the viscosity/EtOH molar content values of 1.2/2.38 and 0.63/3.31.

The adducts of the present invention can be prepared with new methods, not disclosed in the prior art, which are characterized by particular modalities of reaction between MgCl_2 , alcohol, and optionally water.

According to one of these methods $\text{MgCl}_2 \cdot p\text{ROH} \cdot q\text{H}_2\text{O}$ adducts, where R is a C_1 - C_{10} alkyl, $1 \leq p \leq 6$, $0 \leq n \leq 1$, are prepared by dispersing the particles of magnesium dichloride in an inert liquid immiscible with and chemically inert to the molten adduct, heating the system at temperature equal to or higher than the melting temperature of $\text{MgCl}_2 \cdot \text{alcohol}$ adduct and then adding the desired amount of alcohol in vapour phase. The temperature is kept at values such that the adduct is completely melted.

The molten adduct is then emulsified in a liquid medium which is immiscible with and chemically inert to it and then quenched by contacting the adduct with an inert cooling liquid, thereby obtaining the solidification of the adduct.

The liquid in which the MgCl_2 is dispersed can be any liquid immiscible with and chemically inert to the molten adduct. For example, aliphatic, aromatic or cycloaliphatic hydrocarbons can be used as well as silicone oils. Aliphatic hydrocarbons such as vaseline oil are particularly preferred. After the MgCl_2 particles are dispersed in the inert liquid, the mixture is heated at temperatures preferably higher than 125°C and more preferably at temperatures higher than 150°C . Conveniently, the vaporized alcohol is added at a temperature equal to or lower than the temperature of the mixture. Particularly preferred products obtainable with the above specified method are the adducts of formula $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $2 \leq m \leq 4.2$, $0 \leq n \leq 0.7$, and characterized by the specified X-ray diffraction spectrum.

According to another method, the adducts of the invention are prepared by contacting MgCl_2 and alcohol in the absence of the inert liquid dispersant, heating the system at the melting temperature of MgCl_2 -alcohol adduct or above, and maintaining said conditions so as to obtain a completely melted adduct. Said molten adduct is then emulsified in a liquid medium which

is immiscible with and chemically inert to it and finally quenched by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct. In particular, the adduct is preferably kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period equal to or greater than 10 hours, preferably from 10 to 150 hours, more preferably from 20 to 100 hours. Alternatively, in order to obtain the solidification of the adduct, a spray-cooling process of the molten adduct can be carried out.

The catalyst components obtained from the adducts obtained with the above described processes show still more improved properties over the catalyst components prepared by the adducts which have been obtained with the same preparation method but without having been maintained for the requested period of time under the described conditions.

A further method for preparing $\text{MgCl}_2 \cdot p\text{ROH} \cdot q\text{H}_2\text{O}$ adducts, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $2 \leq p \leq 6$, $0 \leq n \leq 1$, comprises reacting the MgCl_2 solid particles and vaporized alcohol in a loop reactor comprising a densified zone in which the particles flow in a densified form under the action of gravity and a fast fluidization zone where the particles flow under fast fluidization conditions. As it is known, the state of fast fluidization is obtained when the velocity of the fluidizing

gas is higher than the transport velocity, and it is characterized in that the pressure gradient along the direction of transport is a monotonic function of the quantity of injected solid, for equal flow rate and density of the fluidizing gas. The terms transport velocity and fast fluidization state are well known in the art; for a definition thereof, see, for example, "D. Geldart, Gas Fluidization Technology, page 155 et seqq., J.Wiley & Sons Ltd., 1986". In the second polymerization zone, where the particles flows in a densified form under the action of gravity, high values of density of the solid are reached (density of the solid = kg of solid particles per m³ of reactor occupied), which approach the bulk density of the adduct; a positive gain in pressure can thus be obtained along the direction of flow, so that it becomes possible to reintroduce the solid particles into the fast fluidization zone without the help of special mechanical means. In this way, a "loop" circulation is set up, which is defined by the balance of pressures between the two zones of the reactor.

In particular, the above method is suitable to prepare $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$ adducts, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $2 \leq m \leq 4.2$, and $0 \leq n \leq 0.7$, characterized by the specified X-ray diffraction spectrum, carrying out the reaction between MgCl_2 particles and vaporized alcohol in the loop reactor, under conditions such

that the vapour pressure of the formed adduct is kept at values lower than 30 mmHg when operating atmospheric pressure. Preferably, the vapour pressure of the adduct is kept at values lower than 25 mmHg and more preferably in the range 10-20 mmHg. Preferably, the reaction between magnesium dichloride and alcohol is carried out in a loop reactor in which the fast fluidization is obtained by a flow of an inert gas, such as nitrogen. The particles of the formed adduct are preferably discharged from the densified zone. As mentioned above, the reaction between magnesium dichloride and alcohol must be carried out under conditions which allow a substantial control of the reaction in order to avoid problems such as melting of the adduct or its substantial dealcoholation. Therefore, the temperature within the reactor, and particularly in the zone where the vaporized alcohol is fed, must be carefully controlled so as to maintain the vapour pressure of the adduct within the above limits. In particular, the control of the temperature is very important in view of the fact that the reaction is greatly exothermic. Therefore, it can be preferred working under conditions such that heat exchange is maximized. For the same reason, the feeding of the alcohol has to be controlled in order to obtain an efficient dispersion of the alcohol in the reactor, thus avoiding the formation of the so called hot spots. The feeding of the alcohol can be carried out

for example with injection nozzles, preferably located in the fast fluidization zone of the loop reactor. According to an alternative method, the alcohol can be fed to the loop reactor in a zone after the densified zone and before the fast fluidization zone, where a centrifugal mixer (of the Loedige type) is installed in order to direct the solid particles towards the walls of the reactor and create a cavitated zone where the alcohol is preferably fed. Preferably, the reactor temperature in correspondence to the alcohol feeding zone should be maintained at values in the range 40-50°C when operating at atmospheric pressure.

The particles of the adduct discharged from the loop reactor can be then subjected to a treatment capable of imparting them a spherical morphology. In particular, the treatment comprises subjecting the adducts to a temperature equal to or higher than the melting temperature of the adduct until the adduct is completely melted, said treatment being carried out in absence or presence of an inert liquid dispersant, then emulsifying the molten adduct in a liquid medium which is immiscible with and chemically inert to it and finally quenching the molten adduct with an inert cooling liquid thereby obtaining the solidification of the adduct in spherical form. Alternatively, in order to obtain the solidification of the adduct in

spherical form, the molten adduct can be subjected to a spray-cooling process according to known techniques.

The treatment which comprises melting the adduct in the presence of an inert dispersant agent, such as vaseline oil, then emulsifying and finally quenching said molten adduct, is particularly preferred.

The liquid in which the molten adduct is emulsified is preferably a hydrocarbon liquid such as vaseline oil. The liquid used to quench the emulsion can be equal to or different from the liquid in which the molten adduct is emulsified. Preferably, it is an aliphatic hydrocarbon and more preferably a light aliphatic hydrocarbon such as pentane, hexane, heptane and the like.

The solid adducts having a spherical morphology are very suitable in the preparation of spherical catalyst components for the polymerization of olefins and in particular for the gas-phase polymerization process.

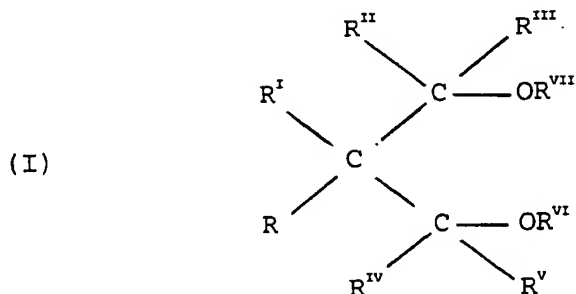
The catalyst components to be used in the polymerization of olefins comprise a transition metal compound of one of the groups IV to VI of the Periodic Table of Elements, supported on the adducts of the invention.

A method suitable for the preparation of said catalyst components, comprises the reaction between the adducts of the invention and the transition metal compound. Among transition

metal compounds particularly preferred are titanium compounds of formula $Ti(OR)_nX_{y-n}$ in which n is comprised between 0 and y; y is the valency of titanium; X is halogen and R is an alkyl radical having 1-8 carbon atoms or a COR group. Among them, particularly preferred are titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates. Preferred specific titanium compounds are $TiCl_4$, $TiCl_3$, $Ti(OBu)_4$, $Ti(OBu)Cl_3$, $Ti(OBu)_2Cl_2$, $Ti(OBu)Cl_2$. Preferably the reaction is carried out by suspending the adduct in cold $TiCl_4$ (generally 0EC); then the so obtained mixture is heated up to 80-130EC and kept at this temperature for 0.5-2 hours. After that the excess of $TiCl_4$ is removed and the solid component is recovered. The treatment with $TiCl_4$ can be carried out one or more times.

The reaction between transition metal compound and the adduct can also be carried out in the presence of an electron donor compound (internal donor) in particular when the preparation of a stereospecific catalyst for the polymerization of olefins is to be prepared. Said electron donor compound can be selected from esters, ethers, amines, silanes and ketones. In particular, the alkyl and aryl esters of mono or polycarboxylic acids such as for example esters of benzoic, phthalic and malonic acid, are preferred. Specific examples of such esters are n-butylphthalate, di-isobutylphthalate, di-n-octylphthalate,

ethyl-benzoate and p-ethoxy ethyl-benzoate. Moreover, can be advantageously used also the 1,3 diethers of the formula:



wherein R^I , R^{II} , R^{III} , R^{IV} , R^V and R^{VI} equal or different to each other, are hydrogen or hydrocarbon radicals having from 1 to 18 carbon atoms, and R^{VII} and R^{VIII} , equal or different from each other, have the same meaning of R^I - R^{VI} except that they cannot be hydrogen; one or more of the R^I - R^{VIII} groups can be linked to form a cycle. The 1,3-diethers in which R^{VII} and R^{VIII} are selected from C_1 - C_8 alkyl radicals are particularly preferred.

The electron donor compound is generally present in molar ratio with respect to the magnesium comprised between 1:4 and 1:20.

Preferably, the particles of the solid catalyst components have substantially spherical morphology and an average diameter comprised between 5 and 150 μm . With the term substantial spherical morphology are meant those particles having a ratio between the greater and smaller axis equal to or lower than 1.5 and preferably lower than 1.3.

Before the reaction with the transition metal compound, the adducts of the present invention can also be subjected to a

dealcoholation treatment aimed at lowering the alcohol content and increasing the porosity of the adduct itself. The dealcoholation can be carried out according to known methodologies such as those described in EP-A-395083. Depending on the extent of the dealcoholation treatment, partially dealcoholated adducts can be obtained having an alcohol content generally ranging from 0.1 to 2.6 moles of alcohol per mole of MgCl_2 . After the dealcoholation treatment the adducts are reacted with the transition metal compound, according to the techniques described above, in order to obtain the solid catalyst components.

The solid catalyst components according to the present invention show a surface area (by B.E.T. method) generally between 10 and 500 m^2/g and preferably between 20 and 350 m^2/g , and a total porosity (by B.E.T. method) higher than 0.15 cm^3/g preferably between 0.2. and 0.6 cm^3/g .

Surprisingly, the catalyst components comprising the reaction product of a transition metal compound with a MgCl_2 -alcohol adduct which is in turn obtained by partially dealcoholating the adducts of the invention, show improved properties, particularly in terms of activity, with respect to the catalyst components prepared from the dealcoholated adducts of the prior art.

The catalyst components of the invention form catalysts for the polymerization of alpha-olefins $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, by reaction with Al-alkyl compounds. The alkyl-Al compound is preferably chosen among the trialkyl aluminum compounds such as for example triethylaluminum, triisobutylaluminum, tri-n-butylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum. It is also possible to use alkylaluminum halides, alkylaluminum hydrides or alkylaluminum sesquichlorides such as AlEt_2Cl and $\text{Al}_2\text{Et}_3\text{Cl}$, optionally in mixture with said trialkyl aluminum compounds..

The Al/Ti ratio is higher than 1 and is generally comprised between 20 and 800.

In the case of the stereoregular polymerization of α -olefins such as for example propylene and 1-butene, an electron donor compound (external donor) which can be the same or different from the compound used as internal donor can be used in the preparation of the catalysts disclosed above. In case the internal donor is an ester of a polycarboxylic acid, in particular a phthalate, the external donor is preferably selected from the silane compounds containing at least a Si-OR link, having the formula $\text{R}_a^1\text{R}_b^2\text{Si}(\text{OR}^3)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1 , R^2 , and R^3 , are alkyl, cycloalkyl or aryl radicals with 1-

18 carbon atoms. Particularly preferred are the silicon compounds in which a is 1, b is 1, c is 2, at least one of R^1 and R^2 is selected from branched alkyl, cycloalkyl or aryl groups with 3-10 carbon atoms and R^3 is a C_1 - C_{10} alkyl group, in particular methyl. Examples of such preferred silicon compounds are methylcyclohexyldimethoxysilane, diphenyldimethoxysilane, methyl-t-butyldimethoxysilane, dicyclopentyldimethoxysilane. Moreover, are also preferred the silicon compounds in which a is 0, c is 3, R^2 is a branched alkyl or cycloalkyl group and R^3 is methyl. Examples of such preferred silicon compounds are cyclohexyltrimethoxysilane, t-butyltrimethoxysilane and hexyltrimethoxysilane.

Also the 1,3 diethers having the previously described formula can be used as external donor. However, in the case 1,3-diethers are used as internal donors, the use of an external donor can be avoided, as the stereospecificity of the catalyst is already sufficiently high.

As previously indicated the components of the invention and catalysts obtained therefrom find applications in the processes for the (co)polymerization of olefins of formula $CH_2=CHR$ in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms.

The catalysts of the invention can be used in any of the olefin polymerization processes known in the art. They can be used for

example in slurry polymerization using as diluent an inert hydrocarbon solvent, or bulk polymerization using the liquid monomer (for example propylene) as a reaction medium. Moreover, they can also be used in the polymerization process carried out in gas-phase operating in one or more fluidized or mechanically agitated bed reactors.

The polymerization is generally carried out at temperature of from 20 to 120°C, preferably of from 40 to 80°C. When the polymerization is carried out in gas-phase the operating pressure is generally between 0.1 and 10 MPa, preferably between 1 and 5 MPa. In the bulk polymerization the operating pressure is generally between 1 and 6 MPa preferably between 1.5 and 4 MPa.

The catalysts of the invention are very useful for preparing a broad range of polyolefin products. Specific examples of the olefinic polymers which can be prepared are: high density ethylene polymers (HDPE, having a density higher than 0.940 g/cc), comprising ethylene homopolymers and copolymers of ethylene with alpha-olefins having 3-12 carbon atoms; linear low density polyethylenes (LLDPE, having a density lower than 0.940 g/cc) and very low density and ultra low density (VLDPE and ULDPE, having a density lower than 0.920 g/cc, to 0.880 g/cc) consisting of copolymers of ethylene with one or more alpha-olefins having from 3 to 12 carbon atoms, having a mole

content of units derived from the ethylene higher than 80%; isotactic polypropylenes and crystalline copolymers of propylene and ethylene and/or other alpha-olefins having a content of units derived from propylene higher than 85% by weight; copolymers of propylene and 1-butene having a content of units derived from 1-butene comprised between 1 and 40% by weight; heterophasic copolymers comprising a crystalline polypropylene matrix and an amorphous phase comprising copolymers of propylene with ethylene and or other alpha-olefins.

The following examples are given to illustrate and not to limit the invention itself.

CHARACTERIZATION

The properties reported below have been determined according to the following methods:

X-ray diffraction spectra were carried out with a Philips PW 1710 instrument using the CuK_α ($\lambda=1,5418\text{\AA}$) with a 40Kv tension generator, a 20mA current generator and a receiving slit of 0.2mm. The X-ray diffraction patterns were recorded in the range between $2\theta=5^\circ$ and $2\theta=15^\circ$ with a scanning rate of $0.05^\circ 2\theta/10$ sec. The instrument was calibrated using the ASTM 27-1402 standard for Silicon. The samples to be analyzed were closed in a polyethylene bag of 50 μm thickness operating in a dry-box.

The DSC measurement were carried out with a METTLER DSC 30 instrument at a scanning rate of 5°C/min in the range 5-125°C. Aluminum capsules having a volume of 40µl filled with the samples in a dry-box were used in order to avoid hydration of the samples.

The viscosity measurement have been carried out according to ASTM D445-65 using a Cannon-Fenske type viscosimeter. During the measurement the samples are maintained in a dry nitrogen environment in order to avoid hydration.

EXAMPLES

General procedure for the preparation of the catalyst component

Into a 1l steel reactor provided with stirrer, 800cm³ of TiCl₄ at 0°C were introduced; at room temperature and whilst stirring 16 g of the adduct were introduced together with an amount of diisobutylphthalate as internal donor so as to give a donor/Mg molar ratio of 10. The whole was heated to 100°C over 90 minutes and these conditions were maintained over 120 minutes. The stirring was stopped and after 30 minutes the liquid phase was separated from the sedimented solid maintaining the temperature at 100°C. A further treatment of the solid was carried out adding 750 cm³ of TiCl₄ and heating the mixture at 120°C over 10 min. and maintaining said conditions for 60 min under stirring conditions (500 rpm). The stirring was then discontinued and after 30 minutes the liquid phase was

separated from the sedimented solid maintaining the temperature at 120°C. Thereafter, 3 washings with 500 cm³ of anhydrous hexane at 60°C and 3 washings with 500 cm³ of anhydrous hexane at room temperature were carried out. The solid catalyst component obtained was then dried under vacuum in nitrogen environment at a temperature ranging from 40-45°C.

General procedure for the polymerization test

A 4 litre steel autoclave equipped with a stirrer, pressure gauge, thermometer, catalyst feeding system, monomer feeding lines and thermostating jacket, was used. The reactor was charged with 0.01 gr of solid catalyst component 0,76 g of TEAL, 0.076g of dicyclopentyl dimethoxy silane, 3.2 l of propylene, and 1.5 l of hydrogen. The system was heated to 70°C over 10 min. under stirring, and maintained under these conditions for 120 min. At the end of the polymerization, the polymer was recovered by removing any unreacted monomers and was dried under vacuum.

EXAMPLE 1

Preparation of the adduct

100 gr of MgCl₂ were dispersed in 1200 cm³ of OB55 vaselin oil into a vessel reactor. The temperature was raised up to 160°C and 135,2 g. of vaporized EtOH having the same temperature were slowly added to the mixture. At the end of the addition, the

mixture was cooled up to 125°C and maintained at this temperature obtaining a completely melted and clear adduct. This mixture was kept at 125° under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000 rpm. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C. The solid particles of the $\text{MgCl}_2 \cdot \text{EtOH}$ adduct recovered, containing 57% by weight of EtOH, were then washed with hexane and dried at 40°C under vacuum.

The X-ray spectrum of the adduct showed in the range of 2 θ diffraction angles between 5° and 15° three diffraction lines present at diffraction angles 2 θ of 8.80° (100), 9.40° (63) and 9.75°(54); the number in brackets represents the intensity I/I₀ with respect to the most intense line.

The DSC profile showed a peak at 100.5°C and a peak at 81.4°C for a total fusion enthalpy of 107.9 J/g. The fusion enthalpy associated with the peak at 81.4°C was 6.9 J/g corresponding to 6.3% of the total fusion enthalpy. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

EXAMPLE 2

100 gr of MgCl_2 were introduced in a vessel reactor which contained 135,2 g of EtOH at room temperature and under stirring. Once the addition of MgCl_2 was completed the temperature was raised up to 125°C and kept at this value for 10 hours.

The so obtained adduct was transferred in a vessel containing 1200 cm^3 of OB55 vaseline oil, and kept at 125°C under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000 rpm for a total time of 20 hours. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C . The solid particles of the $\text{MgCl}_2 \cdot \text{EtOH}$ adduct recovered, containing 57% by weight of EtOH, were then washed with hexane and dried at 40°C under vacuum.

The X-ray spectrum of the adduct showed in the range of 2 θ diffraction angles between 5° and 15° three diffraction lines present at diffraction angles 2θ of 8.83° (100), 9.42° (65) and 9.80° (74); the number in brackets represents the intensity I/I_0

with respect to the most intense line. The DSC profile showed a peak at 103.4°C , a peak at 97.2°C , a peak at 80.1°C and a peak at 70.2°C for a total fusion enthalpy of 101 J/g. The fusion enthalpy associated with the peaks at 80.1°C and at 70.2°C was 16.5 J/g corresponding to 16.3% of the total fusion enthalpy.

The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

EXAMPLE 3

100 gr of MgCl_2 were introduced in a vessel reactor which contained 135,2 g of EtOH at room temperature and under stirring. Once the addition of MgCl_2 was completed the temperature was raised up to 125°C and the system maintained at this temperature and under stirring conditions for 70 hours. The so obtained adduct was transferred in a vessel containing 1200 cm^3 of OB55 vaseline oil, and kept at 125°C under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000 rpm. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C . The solid particles of the $\text{MgCl}_2 \cdot \text{EtOH}$ adduct recovered, containing 57.4% by weight of EtOH, were then washed with hexane and dried at 40°C under vacuum.

The X-ray spectrum of the adduct showed in the range of 2θ diffraction angles between 5° and 15° three diffraction lines present at diffraction angles 2θ of 8.83° (100), 9.42° ($\bar{6}4$) and 9.82° (73); the number in brackets represents the intensity I/I_0 with respect to the most intense line.

The DSC profile showed a peak at 105.7°C, and a peak at 64.6°C for a total fusion enthalpy of 90.3 J/g. The fusion enthalpy associated with the peak at 64.6° was of 0.7 J/g corresponding to 0.77% of the total fusion enthalpy.

The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

EXAMPLE 4

In a loop reactor comprising a fast fluidization zone and a densified zone when the particles flow under the action of gravity were charged 100 g of MgCl_2 . Then, 135.2 g of EtOH vaporized in a oven at 180°C, were conveyed, by a dry nitrogen flow, to the cavitated zone of a Loedige type apparatus placed into the loop reactor after the densified zone and before the fast fluidization zone. The feeding of EtOH was controlled so as to maintain the temperature in the feeding zone in the range between 42 to 48°C. Once the feeding of the alcohol was completed the particles of the adduct were transferred in a vessel containing 1200 cm³ of OB55 vaseline oil, the temperature was raised up to 125°C and the system maintained under said conditions until the adduct became completely melted and clear. This mixture was kept at 125°C under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000

rpm. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C.

The solid particles of the $\text{MgCl}_2 \cdot \text{EtOH}$ adduct recovered, containing 56.5% by weight of EtOH were then washed with hexane and dried at 40°C under vacuum.

The X-ray spectrum of the adduct showed in the range of 2 θ diffraction angles between 5° and 15° three diffraction lines present at diffraction angles 2 θ of 8.90° (100), 9.48° (75) and 9.84° (63); the number in brackets represents the intensity I/I_0 with respect to the most intense line.

The DSC profile showed a peak at 108.2°C, and a peak at 69.1°C for a total fusion enthalpy of 97.7 J/g. The fusion enthalpy associated with the peak at 69.1°C was of 3.1 J/g corresponding to 3.1% of the total fusion enthalpy.

The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

COMPARISON EXAMPLE 5

100 gr of MgCl_2 were dispersed in 1200 cm³ of OB55 vaselin oil into a vessel reactor and 135,2 g of liquid EtOH were added to the mixture. At the end of the addition the temperature was raised up to 125°C and kept at this temperature for 2 hours.

The mixture was kept at 125°C under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000 rpm. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final temperature did not exceed 12°C. The solid particles of the MgCl_2 -EtOH adduct containing 57% by weight of EtOH were then washed with hexane and dried at 40°C under vacuum.

The X-ray spectrum of the adduct showed in the range of 2θ diffraction angles between 5° and 15° four diffraction lines present at diffraction angles 2θ of 8.84° (79.3), 9.2° (100), 9.43° (68.2) and 9.82° (19.5); the number in brackets represents the intensity I/I_0 with respect to the most intense line. The DSC profile showed a peak at 99.8°C, a peak at 82.8°C, and a peak at 71.3°C for a total fusion enthalpy of 107.2 J/g. The fusion enthalpy associated with the peak at 82.8°C and the peak at 71.3°C was of 57.1 J/g corresponding to 53.2% of the total fusion enthalpy. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

EXAMPLE 6

An MgCl_2 -EtOH adduct prepared according to the procedure of Example 2 was thermally dealcoholated until the content of EtOH

reached 44% b.w. Then, the partially dealcoholated adduct was used to prepare, according to the general procedure, the catalyst component which was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

COMPARISON EXAMPLE 7

An MgCl_2 -EtOH adduct prepared according to the procedure of Comparison Example 5 was thermally dealcoholated until the content of EtOH reached 44% b.w. Then, the partially dealcoholated adduct was used to prepare, according to the general procedure, the catalyst component which was then used in a polymerization test carried out according to the procedure described above. The results are reported in Table 1.

EXAMPLE 8

83 gr of MgCl_2 were introduced in a vessel reactor which contained 170 g of EtOH at -19°C and under stirring conditions. Once the addition of MgCl_2 was completed the temperature was raised up to 100°C and kept at this value for 5 hours.

The so obtained adduct was transferred in a vessel containing 1200 cm^3 of OB55 vaseline oil, and kept at 125°C under stirring conditions by means of a Ultra Turrax T-45 type stirrer operating at 2000 rpm for a total time of 10 hours. Thereupon the mixture was discharged into a vessel containing hexane which was kept under stirring and cooled so that the final

temperature did not exceed 12°C. The solid particles of the $\text{MgCl}_2 \cdot \text{EtOH}$ adduct recovered, containing 64% by weight of EtOH, were then washed with hexane and dried at 40°C under vacuum. The DSC profile showed a peak at 100.7°C, and a peak at 56.5°C for a total fusion enthalpy of 103 J/g. The fusion enthalpy associated with the peak at 56.5°C was 12.8 J/g corresponding to 12.4% of the total fusion enthalpy. The catalyst component, prepared according to the general procedure, was tested according to the general polymerization procedure described above and gave the results reported in Table 1.

TABLE 1

Example	Activity	Poured bulk density	Morphological evaluation
1	70	0.43	spherical polymer
2	70	0.43	spherical polymer
3	80	0.45	spherical polymer
4	70	0.43	spherical polymer
comp.5	50	0.40	spherical polymer with breakages
6	40	0.43	spherical polymer
comp.7	35	0.4	spherical polymer
8	60	0.4.	spherical polymer

CLAIMS

1. A $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$ adduct, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $2 \leq m \leq 4.2$, and $0 \leq n \leq 0.7$, characterized by a X-ray diffraction spectrum in which in the range of 2θ diffraction angles between 5° and 15° three diffraction lines are present at diffraction angles 2θ of $8.8 \pm 0.2^\circ$, $9.4 \pm 0.2^\circ$ and $9.8 \pm 0.2^\circ$, the most intense diffraction line being the one at $2\theta = 8.8 \pm 0.2^\circ$, the intensity of the other two diffraction lines being at least 0.2 times the intensity of the most intense diffraction lines.
2. An adduct according to claim 1, wherein $2.2 \leq m \leq 3.8$, and $0.01 \leq n \leq 0.6$ and R is a $\text{C}_1\text{-C}_4$ alkyl.
3. An adduct according to Claim 2, wherein R is ethyl.
4. An adduct according to Claim 3, wherein the intensity of the diffraction lines at $2\theta = 9.4^\circ \pm 0.2^\circ$ and $9.8^\circ \pm 0.2^\circ$ is at least 0.4 times the intensity of the most intense diffraction line.
5. An adduct according to Claim 4, wherein the intensity of the diffraction lines at $2\theta = 9.4^\circ \pm 0.2^\circ$ and $9.8^\circ \pm 0.2^\circ$ is at least 0.5 times the intensity of the most intense diffraction line.
6. An adduct according to claim 3, characterized by a DSC profile in which no peaks are present at temperatures below 90°C or, if peaks are present below said temperature, the

fusion enthalpy associated with said peaks is less than 30% of the total fusion enthalpy.

7. An adduct according to claim 6 which is further characterized by a viscosity value at 125°C which lies, on a plot viscosity vs. EtOH molar content, above the straight line passing through the points having, respectively, a viscosity expressed in poise and a EtOH molar content of 1.2/2.38 and 0.63/3.31.
8. An adduct according to any of the preceding claims, wherein the three diffraction lines at $2\theta = 8.8^\circ \pm 0.2^\circ$, $9.4^\circ \pm 0.2^\circ$ and $9.8^\circ \pm 0.2^\circ$ are the three main diffraction lines in the range of 2θ diffraction angles between 5° and 15° .
9. A $\text{MgCl}_2 \cdot m\text{ROH} \cdot n\text{H}_2\text{O}$ adduct, where R is a C_2 - C_{10} alkyl, $2 \leq m \leq 4.2$, and $0 \leq n \leq 0.7$, characterized by a DSC profile in which no peaks are present at temperatures below 90°C or, if peaks are present below said temperature, the fusion enthalpy associated with said peaks is less than 30% of the total fusion enthalpy.
10. An adduct according to Claim 9, wherein R is a C_1 - C_4 alkyl, $2.5 \leq m \leq 3.5$, and $0 \leq n \leq 0.4$.
11. An adduct according to Claim 9, wherein R is ethyl.
12. An adduct according to Claim 9, wherein if peaks in the DSC profile are present at temperatures below 90°C, the fusion enthalpy associated with said peaks is less than 10% of the

total fusion enthalpy, and wherein the maximum peak occurs at temperatures between 95 and 115°C.

13. An adduct according to any of the preceding claims, in the form of spherical particles.
14. A catalyst component for the polymerization of olefins comprising the product of the reaction between a transition metal compound and an adduct according to any of the preceding claims.
15. A catalyst component for the polymerization of olefins comprising the product of the reaction between a transition metal compound and an MgCl_2 -alcohol adduct, said adduct being obtainable by partially dealcoholating an adduct according to any of the preceding claims.
16. A catalyst component for the polymerization of olefins according to claim 15 in which the partially dealcoholated adduct contains from 0.1 to 2.6 moles of alcohol per mole of MgCl_2 .
17. A catalyst component for the polymerization of olefins according to claims 14 to 16 in which the transition metal compound is a titanium compounds of formula $\text{Ti}(\text{OR})_n\text{X}_{y-n}$ in which n is comprised between 0 and y; y is the valency of titanium; X is halogen and R is an alkyl radical having 1-8 carbon atoms or a COR group.

18. A catalyst component for the polymerization of olefins according to claim 17 in which the transition metal compound is a titanium compounds having at least one Ti-halogen bond such as titanium tetrahalides or halogenalcoholates.
19. A catalyst component for the polymerization of olefins according to one of the claims 18 comprising an electron donor compound.
20. A catalyst component for the polymerization of olefins according to claim 19 in which the electron donor compound is selected from ethers, amines, silanes and ketones.
21. A catalyst component for the polymerization of olefins according to claim 20 in which the electron donor compound is selected from alkyl and aryl esters of mono or polycarboxylic acids.
22. Catalyst for the polymerization of olefins comprising the product of the reaction between a catalyst component according to one of the claims 14 to 21, and an aluminum alkyl compound.
23. Catalyst for the polymerization of olefins according to claim 22 in which the aluminum compound is a Al-trialkyl compound.
24. Catalyst for the polymerization of olefins according to claim 22 further comprising an external donor.

25. Catalyst for the polymerization of olefins according to claim 24 in which the external donor is selected from the silane compounds containing at least a Si-OR link, having the formula $R_1^1 R_2^2 Si(OR^3)_c$, where a and b are integer from 0 to 2, c is an integer from 1 to 3 and the sum (a+b+c) is 4; R^1 , R^2 , and R^3 , are alkyl, cycloalkyl or aryl radicals with 1-18 carbon atoms.
26. Process for the polymerization of olefins of formula $CH_2=CHR$, in which R is hydrogen or a hydrocarbon radical having 1-12 carbon atoms, carried out in the presence of a catalyst according to one of the claims 22-25.
27. Process for the preparation of $MgCl_2 \cdot pROH \cdot qH_2O$ adducts, where R is a C_1-C_{10} alkyl, $1 \leq p \leq 6$, and $0 \leq n \leq 1$, comprising:
- dispersing the particles of magnesium dichloride in an inert liquid immiscible with and chemically inert to the molten adduct;
 - heating the system at a temperature equal to or higher than the melting temperature of the adduct;
 - adding the alcohol in vapour phase maintaining the temperature at values allowing the adduct is completely melted;
 - emulsifying the molten adduct in a liquid medium which is immiscible with and chemically inert to said adduct;

- quenching the emulsion by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct.
28. Process according to claim 27 in which $2 \leq p \leq 4.2$ and $0 \leq n \leq 0.7$.
29. Process according to claim 28 characterized in that the liquid in which the $MgCl_2$ particles are dispersed is selected from the group consisting of aliphatic, aromatic or cycloaliphatic hydrocarbons and silicone oils.
30. Process according to claim 29 characterized in that the liquid in which the $MgCl_2$ particles are dispersed is selected from the group consisting of aliphatic hydrocarbons such as vaseline oil.
31. Process according to claim 30 characterized by heating the system at temperatures higher than $125^\circ C$ and more preferably to temperature higher than $150^\circ C$.
32. Process according to claim 31 in which the vaporized alcohol is added at a temperature equal to or lower than the temperature of the mixture.
33. Process according to claim 32 characterized in that the liquid medium in which the molten adduct is emulsified is a hydrocarbon liquid such as vaseline oil.

34. Process according to claim 33 characterized in that the liquid used to quench the emulsion is an aliphatic hydrocarbon such as pentane, hexane, heptane.
35. Process for the preparation of an adduct according to claim 1 comprising :
- contacting $MgCl_2$ and alcohol in the substantial absence of an inert liquid dispersant;
 - heating the system at a temperature equal to or higher than the melting temperature of the adduct and maintaining the temperature at values allowing the adduct is completely melted;
 - emulsifying the molten adduct in a liquid medium which is immiscible with and chemically inert to said adduct;
 - quenching the emulsion by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct.
36. Process for the preparation of an adduct according to claim 1 comprising :
- contacting $MgCl_2$ and alcohol in the substantial absence of an inert liquid dispersant;
 - heating the system at a temperature equal to or higher than the melting temperature of the adduct and maintaining the temperature at values allowing the adduct is completely melted;

- spray-cooling the said molten adduct thereby obtaining the solidification of the adduct.

37. Process according to claims 35 or 36 said process being characterized by the fact that the adduct is kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period greater than 10 hours.
38. Process according to claim 37 in which the adduct is kept at a temperature equal to or higher than its melting temperature, under stirring conditions, for a time period of from 10 to 150 hours.
39. Process for the preparation of $\text{MgCl}_2 \cdot p\text{ROH} \cdot q\text{H}_2\text{O}$ adducts, where R is a $\text{C}_1\text{-C}_{10}$ alkyl, $1 \leq p \leq 6$, and $0 \leq n \leq 1$, which comprises reacting MgCl_2 solid particles and vaporized alcohol in a loop reactor comprising a densified zone in which the particles flow in a densified form under the action of gravity and a fast fluidization zone where the particles flow under fast fluidization.
40. Process according to claim 39 in which the fluidization is obtained by a flow of an inert gas, such as nitrogen, and in which the particles of magnesium dichloride-alcohol adduct are discharged from the densified zone.

41. Process according to claim 40 in which the feeding of the alcohol is carried out with injection nozzles located in the fluidization zone of the loop reactor.
42. Process according to claim 40 in which the alcohol is fed to the loop reactor in a zone after the densified zone and before the fluidization zone.
43. Process according to claim 42 in which the alcohol is fed into the cavitated zone created by a Loedige type apparatus located in the loop reactor in a zone after the densified zone and before the fluidization zone.
44. Process according to claim any of the claims 39-43 in which $2 \leq p \leq 4.2$, and $0 \leq n \leq 0.7$, said process being carried out under conditions such that the vapour pressure of the formed adduct is kept at values lower than 30 mmHg when operating at atmospheric pressure.
45. Process according to claim 44 in which the vapour pressure of the adduct is kept at values lower than 25 mmHg and more preferably in the range 10-20 mmHg.
46. Process according to claim 45 in which the temperature within the reactor in correspondence of the alcohol feeding zone is kept in the range of from 40 to 50°C.
47. Process according one of the claims 39-46 further comprising:

- heating the particles of the adduct discharged from the loop reactor at a temperature equal to or higher than the melting temperature of the adduct and maintaining the temperature at values such that the adduct is completely melted;
- emulsifying the molten adduct in a liquid medium which is immiscible with and chemically inert to said adduct;
- quenching the emulsion by contacting the adduct with an inert cooling liquid thereby obtaining the solidification of the adduct.

48. Process according one of the claims 39-46 further comprising:

- heating the particles of the adduct discharged from the loop reactor at a temperature equal to or higher than the melting temperature of the adduct and maintaining the temperature at values such that the adduct is completely melted;
- spray-cooling the molten adduct thereby obtaining the solidified adduct.

INTERNATIONAL SEARCH REPORT

i. National Application No
PCT/EP 98/01680

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08F4/02 C08F10/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 400 333 A (HIMONT INC) 5 December 1990 see page 4, line 7 - line 12 ---	35
X	EP 0 713 886 A (JAPAN POLYOLEFINS CO LTD) 29 May 1996 see table 1 see example 1 ---	35
X	EP 0 412 696 A (NESTE OY) 13 February 1991 see page 5, line 16 - line 30 ---	36
X	WO 93 11164 A (NESTE OY) 10 June 1993 see page 13, line 25 - line 35 ---	36
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
"&" document member of the same patent family

Date of the actual completion of the international search

5 August 1998

Date of mailing of the international search report

21/08/1998

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Fischer, B

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 98/01680

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 11166 A (NESTE OY) 10 June 1993 see claim 1 see page 7, line 36 - page 8, line 8 see example 1 ---	36
X	EP 0 700 936 A (CHISSO CORP) 13 March 1996 see page 10, line 16 - line 40 -----	36

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/01680

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0400333	A	05-12-1990	AT 130014 T	15-11-1995
			AU 634229 B	18-02-1993
			AU 5457090 A	01-11-1990
			CA 2015683 A	28-10-1990
			CN 1047514 A	05-12-1990
			CZ 9002110 A	13-08-1997
			DE 69023392 D	14-12-1995
			DE 69023392 T	15-05-1996
			ES 2081870 T	16-03-1996
			FI 99016 B	13-06-1997
			IL 94153 A	21-10-1994
			JP 3205439 A	06-09-1991
			MX 20476 A	01-12-1993
			NO 176442 B	27-12-1994
			PL 164127 B	30-06-1994
			PT 93922 A,B	20-11-1990
			RU 2092502 C	10-10-1997
			US 5302454 A	12-04-1994
EP 0713886	A	29-05-1996	JP 8143615 A	04-06-1996
EP 0412696	A	13-02-1991	FI 893621 A	29-01-1991
			AT 131499 T	15-12-1995
			CA 2021196 A	29-01-1991
			DE 69024128 D	25-01-1996
			DE 69024128 T	20-06-1996
			JP 3066704 A	22-03-1991
			NO 173656 C	12-01-1994
			US 5322830 A	21-06-1994
WO 9311164	A	10-06-1993	FI 915630 A	30-05-1993
			EP 0614466 A	14-09-1994
			JP 7501568 T	16-02-1995
			NO 941970 A	26-05-1994
WO 9311166	A	10-06-1993	CA 2124572 A	10-06-1993
			FI 915632 A,B	30-05-1993
			EP 0614467 A	14-09-1994
			NO 941874 A	19-05-1994
			US 5468698 A	21-11-1995

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 98/01680

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9311166 A		DE 69208265 D	21-03-1996
		DE 69208265 T	04-07-1996
EP 0700936 A	13-03-1996	JP 8127616 A	21-05-1996
		JP 8127615 A	21-05-1996